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THE PRODUCTION OF HAFNIUM AT Y-12

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THE PRODUCTION OF HAFNIUM AT Y-12

I. INTRODUCTION

As authorized by the Atomic Energy Commission, hafnium tailings collected from the zirconium extraction plant from May 1, 1950 until March 25, 1951 were re-run in order to concentrate the hafnium to a minimum of 95%, basis total metals. Based on 2% contained hafnium in the crude tetrachloride feed, a quantity of approximately 5,500 pounds of hafnium was expected. Because no precise analytical methods had been developed for the analysis of hafnium, an exact measure of the quantity was not possible. Estimated gross weight of the collected hydroxide cake and analyses of spot samples indicated that the quantity available should be approximately 5,000 pounds. Assuming that 80% recovery could be obtained during processing, the Commission was informed that we would expect to recover approximately 4,000 pounds of hafnium as hafnium tetrachloride.

After rewashing the hafnium hydroxide cake to remove sulphates, the estimated net weight and spot analyses still indicated in excess of 5,000 pounds of contained hafnium. The washed cake was dissolved for feed to the extraction plant. Analyses of the solutions indicated that an excess of 4,000 pounds of hafnium was fed to the extraction system.

After processing, 1,229 pounds of hafnium was recovered as refined oxide with 226 pounds being left in the plant tailings. There are only two possible explanations for this significantly reduced recovery, (1) the original zirconium tetrachloride feed solution did not contain 2% hafnium, and/or (2) processing losses were much greater than had been anticipated. Measured discards were approximately fifty pounds and estimated losses during the repurification were less than 350 pounds; this estimate is considered a maximum. An analytical investigation of the quantity of contained hafnium in the zirconium tetrachloride feed is being made. A review of the overall operation including precautions taken to minimize losses follows.

II. DESCRIPTION OF PROCESS

During the period of collection the sulphuric acid scrubber solution containing the hafnium tailings was precipitated with ammonium hydroxide and the resulting hydroxide cake containing approximately 10% sulphates was stored in iron drums. During the extraction plant shutdown in April, sulphate removal was effected by slurrying with dilute ammonium hydroxide and filtering. Careful washing techniques were employed to give adequate washing in the press. The cake was then transferred to Building 9211 for storage. After the repair of the extraction plant was completed, the cake was transferred into 250 gallon glass-lined, steam-jacketed reactors and dissolved in hydrochloric acid. A small amount of ammonium thiocyanate was added at this step to partially reduce the iron present so that the separation of iron in the extraction plant would be in favor of the zirconium rather than the hafnium stream. The initial dissolution gave a solution analyzing 0.4 - 0.5 pounds of contained metals per gallon. After about 65% of this material was processed, the remaining solutions were evaporated in the reactors to a concentration of approximately 0.6 - 0.7 pounds per gallon. This operation was added in order to increase the capacity of the extraction plant. The sulphuric acid scrubber solution containing the hafnium and the hydrochloric acid solution containing the zirconium were precipitated with ammonium hydroxide in separate locations. Resulting slurries were filtered through 18" plate and frame filter presses. The hafnium hydroxide cake was transferred to Room 36, Building 9206 and the sulphates removed by re-slurrying in the precipitation reactors, dissolved in hydrochloric acid and the resulting solution filtered to remove insolubles. Filtrate from this operation was precipitated with salicylic acid and the cake collected in the 36" filter presses. The cake was transferred to Building 81-10 and burned to the oxide.

III. POSSIBLE SOURCES OF PROCESSING LOSSES

A. Original Collection of Hafnium Tailings

The sulphuric acid scrubber solution containing the hafnium tailings was originally collected in a 1,500 gallon rubber-lined rectangular tank. The acid solution was precipitated with ammonium hydroxide with agitation being provided by means of two agitators. Ammonia was added continuously beneath the surface of the liquor with a piston-type proportioning pump. Prior to filtration, the pH of the solution was checked to insure that precipitation was complete. There is no theoretical reason for

expecting this precipitation not to be quantitative. The alkaline slurry was pumped through an 18" open discharge plate and frame filter press, with the filtrate being discharged to the sewer. The filter press was packed with Vinyon N filter cloth and sharkskin polishing paper. Spot weighings and total number of drums collected indicated that over 90,000 pounds of cake was collected; spot analyses indicated that contained hafnium was approximately 5,000 pounds. Possibility for losses in this operation are as follows:

(1) Failure to completely neutralize the solution:

Since the pH of the solution was checked prior to filtration, and since the line used during this operation was of iron construction, it is believed that this possibility can be ruled out. The iron line gave satisfactory service for the entire collection period.

(2) Pumping solution to sewer without going through the filter press:

This was not possible without changing the equipment.

(3) Improper filtration:

Experience has shown that the type of filter being used gave adequate separation of solids from the slurry. There is, of course, the possibility that the filter press was not packed properly; however, it should be pointed out that personnel responsible were experienced in this operation, and that the importance of quantitative collection was emphasized throughout the program.

(4) Losses in storage:

The hydroxide cake was stored in black iron drums. Because of a shortage of storage space and deterioration of the black iron drums due to corrosion from ammonium sulphate solution left after the excess ammonia evaporated, approximately one half of the cake was transferred to an open concrete tank in the S-2 area. It is believed that losses in storage and transfer were negligible.

It is our opinion that losses during the hafnium collection and storage operation did not exceed a maximum of 10% and that they were probably considerably lower than this.

B. Rewashing to Remove Sulphates

During the three-week plant shutdown the hafnium hydroxide cake was rewashed in the purification equipment located in Building 9206, Room 36, to remove sulphates prior to processing through extraction. The cake was slurried with dilute ammonium hydroxide in the existing reactors and filtered in the 36" filter presses. This operation was carried out carefully and no significant losses are believed to have occurred. Net weight obtained, based on drum weights and a count of the total number of drums, indicated approximately 79,000 pounds of cake was present. Spot samples taken on a few drums indicated that this material should contain in excess of 5,000 pounds of hafnium. In view of the loss of weight due to sulphate removal, this quantity of wet cake is considered to check well with the estimated weight fed into the operation.

C. Dissolution of Washed Hafnium Hydroxide Cake

Possibilities for losses in this operation are as follows:

(1) Spillage of cake while transferring into the reactor:

This operation was done carefully and since any spilled cake would be readily apparent, it is considered that losses here are negligible.

(2) Solution filtration:

This operation was also done in a careful manner and solutions leaking from the press were returned for re-filtration. Filtration presented no operational problems and the quantity that leaked out was slight. Losses here are considered negligible.

(3) Broken and leaky lines, etc.:

No solutions were spilled as a result of broken lines. A few leaks were occasioned in the system but quantity of solution lost was insignificant.

D. Extraction Plant

The following possibilities for losses were occasioned during the operation of the extraction plant:

(1) Leaks through the system:

While a number of leaks developed during the operation of this system, the quantities involved were very minor, and it is considered that losses from this source are negligible. When necessary to drain columns to repair valves or leaks, solution was collected and transferred back into the system.

(2) Loss of hexone from the overflow tank:

The high concentration of iron in the system resulted in some difficulties in plant operation. It was very difficult to determine interfaces in the columns and there was some flooding and syphoning. As a result of this, some of the hexone from the overflow tank was discharged to the sewer. Assuming the worst possible conditions from the standpoint of loss, the maximum hafnium loss from this source is estimated to be 250 pounds. Actual losses are considered to be much lower.

(3) Spillage, trap drainings, etc.:

This was kept to a minimum and it is believed that the maximum possible loss here did not exceed fifty pounds; actual losses were much lower.

(4) Collection of hafnium and zirconium solutions:

Both hafnium product and zirconium tailings were precipitated with ammonium hydroxide and filtered through 18" plate and frame filter presses. Prior to filtration, pH of solution was checked to insure that the slurry was alkaline. While there is no theoretical reason why this procedure should not be quantitative, filtrates were analyzed and the filtrate analytical procedure was checked. This investigation indicated that the reaction was quantitative. Total hafnium contained in the filtrates by analysis was less than five pounds.

During the whole period of operation of the extraction plant personnel were aware of the necessity of keeping losses to a minimum. It should be pointed out that in similar operation for the production of zirconium, overall losses through the extraction facility were less than 5%.

E. Purification

Possibility of losses in this operation are as follows:

(1) Rewashing of hafnium hydroxide cake to remove sulphates:

This operation was carried out under close supervision in the same manner as outlined for washing the raw cake prior to dissolution for extraction plant feed. Total quantity contained in the wash solution calculated from reported analytical values was less than 6.5 pounds. Each sample was reported as containing less hafnium than could be detected by the analytical method.

(2) Precipitation with salicylic acid:

This operation was carried out using the same procedure as for the recovery of zirconium. All filtrates were analyzed and, based on this analysis forty pounds of hafnium were discarded with the filtrate. Recovery through this operation, based on this data, was 97% which is equivalent to what would be expected and what is normally obtained during zirconium production.

F. Burning

Burning operations at Building 81-10 were carried out on the day shift only, under careful supervision. The burners were turned off at the end of the shift and the oxide unloaded from cool trays. Calculated losses were thirty-nine pounds. The total recovery of hafnium through purification and burning is 94.2% which compares favorably with the 92.2% normally obtained during zirconium production.

III. SUMMARY OF OPERATING DATA

A. Basis for Estimated Quantity of Hafnium

- (1) Estimated quantity of hafnium fed to extraction plant
based on recovered zirconium, assuming 2% feed - 5,665 lbs.
- Shipment of hafnium tailings authorized by AEC 105
Contained hafnium in zirconium product 56
- Net hafnium in tailings 5,504 lbs.
- (2) Estimated quantity of hafnium contained in
90,000 - 100,000 lbs. wet cake - 5,000 lbs.
(Spot weights and spot analysis)
- (3) Estimated quantity of hafnium contained in
washed wet cake - 5,600 lbs.
(Spot weights and spot analysis)

In view of the unknown disposition of the hafnium tailings during most of the collection period, the expense and manpower required to develop adequate analytical procedures were not deemed justified. Estimates determined, as outlined above, were considered to be in good agreement.

Hafnium - Zirconium Material Balance - Extraction PlantBasis of Recovery Measurements -
Analyzed Product Solutions

Lbs. Hf	Lbs. Zr	Lbs. Ammonia Precipitables as Calined Oxide
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Feed to Extraction Plant (Basis - Analysis of Dissolved Cake)	4,013	2,198	9,555
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Recovery From Extraction Plant
(Basis - Weighed Analyses of
Spot Samples From Product
Streams)

Hafnium Stream	1,864	39	2,273
Zirconium Stream	123	2,873	4,104

Tailings (Solid)	82	107	344
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Estimated Losses (Maximum)	300	300	800
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Total Accounted For	2,369	3,319	7,521
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Difference	-1,644	1,121	-2,034
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Basis of Recovery Measurements -
Analyzed Wet Cake From Ammonium Hydroxide
Precipitation of Product Solutions

Lbs. Hf	Lbs. Zr	Lbs. Ammonia Precipitables as Calined Oxide
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Feed to Extraction Plant (Basis - Analysis of Dissolved Cake)	4,013	2,198	9,555
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Recovery From Extraction Plant
(Basis - Analyzed Hydroxide Cake)

Hafnium Hydroxide Cake	1,486	35	1,858
Zirconium Hydroxide Cake	106	2,436	3,530

Tailings (Solid) (Solution)	82	107	344
	5	-	100

Estimated Losses (Maximum)	300	300	800
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Total Accounted For	1,979	2,878	6,632
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Difference	-2,034	680	-2,923
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Analysis of Data

- (1) Hafnium - zirconium material balance indicates that analytical difficulties exist in obtaining accurate measurements, particularly in the middle ranges as represented by the feed solutions.
- (2) Differences between quantity of product as measured by the analyses of the product solutions and as measured by analyses of the hydroxide cakes are greater than anticipated. Our previous experience indicates that it is difficult to obtain a representative sample of the wet hydroxide cakes; however, quantity of hafnium measured here agrees reasonably well with the quantity later measured in the purification step. Analyses of alkaline filtrates from the ammonium hydroxide precipitation of the hafnium tailings indicates that the operation was essentially quantitative.
- (3) Material balance around the ammonia precipitables shows greater discrepancy than had been anticipated. It is our opinion that the difference is not accounted for by processing losses; estimated losses tabulated are based on the best available information and are considered a maximum.

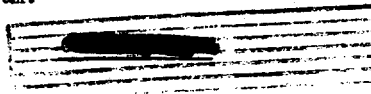
C. Hafnium Material Balance - Purification Plant & Burning

	<u>Lbs. Contained Hafnium</u>
<u>Feed</u>	
(1) Basis analyzed hafnium hydroxide cake	1,455*
(2) Basis analyzed hafnium hydroxide cake after washing 1,441 Analysis of wash solution <u>6.5</u>	
Total	1,447.5
(3) Analyzed dissolved solution	1,308
(4) Analyzed filtrate and wash from salicylic acid precipitation	40
(5) Net calculated pounds in hafnium salicylate	1,268
Net pounds analyzed in calcined oxide	1,229
Calculated burner losses	39

Analysis of Data

- (1) Because of inherent imprecision in sampling wet hydroxide cake, quantities measured by the methods outlined above are considered to be reasonably good agreement.
- (2) Measured recovery through these operations compares favorably with experience in zirconium production through the same equipment.

* This is the hafnium content of the hafnium hydroxide cake corrected for titanium.



IV. QUALITY OF PRODUCT

As pointed out to the Commission prior to starting processing, iron and titanium averaged about 700 ppm and 8,000 ppm, respectively. With the exception of boron and silica on one batch representing 161 pounds of hafnium, the impurity level is of the same general order of magnitude as is obtained for zirconium oxide. Boron and silica were reported as 25 ppm and 600 ppm, respectively. Future processing to the metal should result in adequate purification of these elements.

The average zirconium content of 1.6% is less than the guaranteed 5%. Zirconium analysis on each batch produced is tabulated below:

<u>Batch No.</u>	<u>Net Weight, Lbs.</u>	<u>Contained Hf, Lbs.</u>	<u>Contained Zr, %</u>
1	304	244	0.8
2	289	229	0.9
3	350	269	3.0
4	154	119	3.0
5	260	207	1.2
6	201	161	1.2
Total		1,229	